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Carboxylation of Olefins with Carbon Monoxide Using Various Strong Acids-H_2O-Group 1B Metal Carbonyl Catalyst Systems

Norihiko Yoneda,* Tsuyoshi Fukuhara, Yukio Takahashi, and Akira Suzuki

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060

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Carboxylation of 2,4,4-trimethyl-1-pentene and 1-octene with carbon monoxide was studied in the presence of various strong acids–H_2O–Cu(I) carbonyl catalyst systems in an attempt to find a practical method for the preparation of carboxylic acids. The reaction takes place smoothly at room temperature to give tertiary acids in higher yields than that with the use of sulfuric acid. The procedure is preferable for the ready separation of products from the catalyst layer without quenching by water.

An interesting carboxylation procedure of olefins and alcohols using Cu(I) carbonyl catalyst in the presence of concentrated sulfuric acid has been demonstrated by Souma *et al.*[1] The procedure gives tertiary carboxylic acids in high yields under milder conditions than those of the Koch-Haaf reaction.[2] However, in order to isolate the products, it is necessary to quench the reaction system by adding a large amount of water which leads to the destruction of the catalyst. It was considered that the reaction in strong acids having a water molecule as its component might facilitate the formation of carboxylic acid without the addition of a water molecule at the end of the reaction. We thus investigated extensively the catalytic behavior of Cu(I) carbonyl in the presence of strong acids such as BF_3–H_2O, BF_3–H_3PO_4–H_2O, HF–H_2O and so on. Some of these catalyst systems were found not only to show very high activity on the carboxylation of olefins but also to separate products readily from the reaction mixture with use of a co-solvent such as cyclohexane and chlorobenzene without quenching by intentional addition of water.[3]

Further details of these reaction behaviors will be described hereinafter.

Experimental

Materials. Commercial copper(I) oxide, silver monoxide, boron trifluoride and carbon monoxide of the highest purity were used without further purification. Olefins and organic solvents were purified in the usual way. Distilled hydrogen fluoride was used. BF_3–H_2O complex was prepared by introducing BF_3 gas into water cooled with ice. The desired complexes with given BF_3/H_2O mole ratios could be obtained by adjusting the amount of BF_3 absorbed.[4]

General Procedure of Carboxylation. A solution of Cu_2O (2 g, 14 mmol) in 40—50 g of strong acid was placed in a 200 ml galss reaction vessel fitted with a thermometer and a reflux condenser. Carbon monoxide was then introduced into the reaction mixture under thorough stirring with a magnetic stirrer at a constant flow rate of 20 ml/min to obtain Cu(I) carbonyl at the desired temperature. After complete carbon monoxide absorption, *i.e.*, the completion of cuprous carbonyl formation, 100 mmol of olefin (2,4,4-trimethyl-1-pentene or 1-octene) with or without 50 ml of an appropriate organic solvent was added dropwise by introducing an excess amount of carbon monoxide at a fixed temperature.

A polyethylene reaction vessel was used in the case of HF. All the work was conducted in a well-shielded fume hood.

After completion of the reaction, the reaction mixture separated into two layers, the upper usually being an organic layer and the lower a catalyst layer. The catalyst layer was then hydrolyzed with ice-water and organic materials were extracted with ether. In the case of a recycle experiment of the catalyst, the catalyst layer separated out from the organic layer was subjected to the next run without any treatment.

The yield of individual acids such as 2,2-dimethylpropanoic, tertiary C_6—C_8, tertiary C_9 and polymeric (mainly C_{13} acids) was determined by VPC.[4] The analysis was carried out with a Shimadzu 3AH apparatus, fitted with a 3 m×3 mm column packed with ethylene glycol succinate–H_3PO_4 at 170 °C. C_9 and C_{13} acids produced by Shell Oil Company were used as references. Tertiary C_6—C_8 acids were synthesized by the Grignard reaction from the corresponding alkyl halides.

The amount of Cu^+ in the organic layer was analyzed as Cu^{2+} after oxidation with the air by the atomic absorption spectroscopic method.

Results and Discussion

Group IB Metal Carbonyl Complex Formation in Various Acid Systems. A Stream of Carbon monoxide was

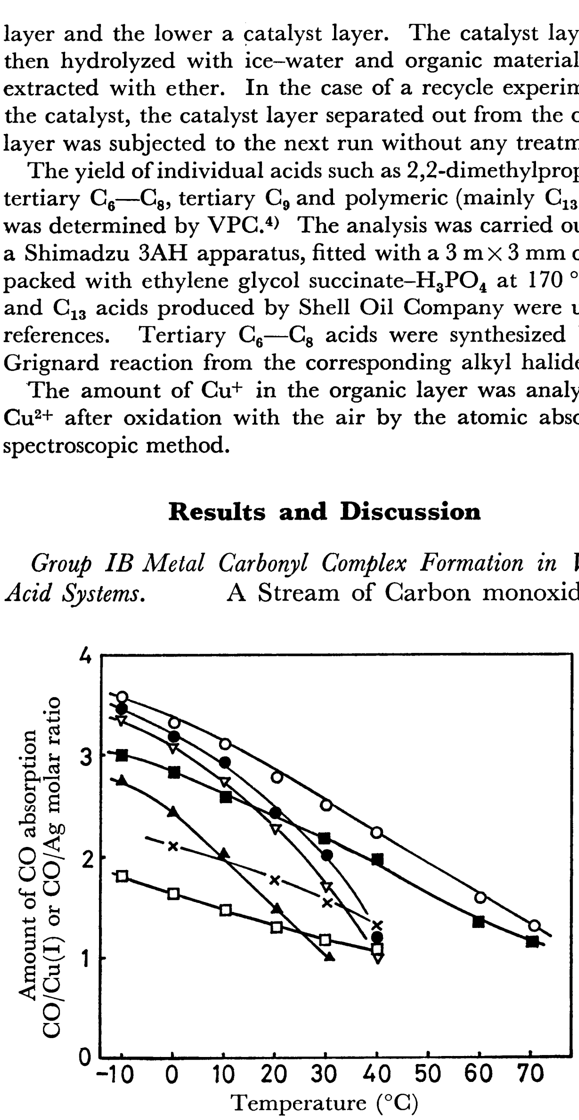


Fig. 1. Temperature dependence of CO absorption in various strong acid–H_2O–Cu_2O (Ag_2O) system.
Amount of Cu_2O; 14 mmol.
Amount of Ag_2O; 14 mmol.
Amount of acid–H_2O; 40 g.
-○- BF_3–H_3PO_4(85%)–H_2O–Cu_2O; $BF_3/H_3PO_4/H_2O$ =1/1.1/1. -●- BF_3–HF–H_2O–Cu_2O; BF_3/HF/H_2O =0.9/6.8/1. -▽- HF–H_2O–Cu_2O; HF/H_2O=9/1. -■- BF_3–H_2O–Cu_2O; BF_3/H_2O=0.9/1. -▲- HF–H_2O–Cu_2O; HF/H_2O=6/1. -×- BF_3–H_2SO_4(70%)–H_2O–Cu_2O; $BF_3/H_2SO_4/H_2O$=1/0.4/1. -□- BF_3–H_2O–Ag_2O; BF_3/H_2O=0.9/1.

TABLE 1. CARBOXYLATION OF TRIMETHYLPENTENE USING STRONG ACID–H_2O–$M(CO)_n^+$ [a)] SYSTEM

Strong acid–H_2O–$M(CO)_n^+$ system	Reaction temp (°C)	Organic solvent	Product distribution (%)		Total yield of acid (%)
			In org. layer	In cat. layer	
BF_3–H_2O–Cu_2O 0.9: 1	30	Cyclohexane	53	47	96
BF_3–H_2O–Cu_2O 0.9: 1	30	Chlorobenzene	88	12	93
BF_3–H_2O–Cu_2O 0.7: 1	30	Cyclohexane	90	10	55
BF_3–85%H_3PO_4–Cu_2O	20	Cyclohexane	21	79	77
BF_3–85%H_3PO_4–Cu_2O	20	Chlorobenzene	30	70	80
BF_3–50%H_2SO_4–Cu_2O	30	Cyclohexane	28	72	81
BF_3–50%H_2SO_4–Cu_2O	30	Chlorobenzene	71	29	83
HF–H_2O–Cu_2O[b)] 11.4: 1	18	Cyclohexane	45	55	98
HF–H_2O–BF_3–Cu_2O 6.8: 1: 0.9	18	Cyclohexane	12	88	99
HF–H_2O–BF_3–Cu_2O 6.8: 1: 0.9	18	Chlorobenzene	15	85	95
BF_3–H_2O–Ag_2O 0.9: 1	20	Chlorobenzene	95	5	78
BF_3–H_2O–Ag_2O[c)] 0.9: 1	20	Cyclohexane	44	56	80
96% H_2SO_4–Cu_2O[d)]	20	Cyclohexane	7	93	40
96% H_2SO_4–Cu_2O[d)]	20	Chlorobenzene	30	70	40
BF_3–H_2O–Cu_2O[e)] 0.9: 1	20	Cyclohexane	100	—	73

a) Reaction conditions: BF_3, 0.50 mol; Cu_2O, 14 mmol; organic solvent, 50 ml; trimethylpentene, 0.1 mol. b) H_2O, 0.55 mol. c) Ag_2O, 7 mmol. d) 96% H_2SO_4, 40 g. e) 1-Octene, 0.10 mol.

passed through a solution of Cu_2O in various acids at −10—70 °C. The results are shown in Fig. 1.

Remarkable absorption of carbon monoxide was observed in acid media such as BF_3–H_3PO_4–H_2O (molar ratio, 1: 0.9: 0.1), BF_3–HF–H_2O (0.9: 6.8: 1), HF–H_2O (9: 1) and BF_3–H_2O (0.9: 1), as compared with that in concentrated sulfuric acid.[1)] Even in HF–H_2O of molar ratio 6: 1, about 3 mol of carbon monoxide was absorbed per one mol of Cu(I) at −10 °C.

As described by Souma and Sano,[1,5)] the unstable tricarbonylcopper(I) cation $Cu(CO)_3^+$ formed in acid media acts as a catalyst for the carboxylation of olefins under atmospheric pressure. The active species $Cu(CO)_3^+$ can be considered to show the following equilibrium. The species carbonylcopper(I) cation, $Cu(CO)^+$, shows no catalytic behavior for the carboxylation reaction.[1)]

$$Cu(CO)_3^+ \rightleftharpoons Cu(CO)^+ + 2CO$$

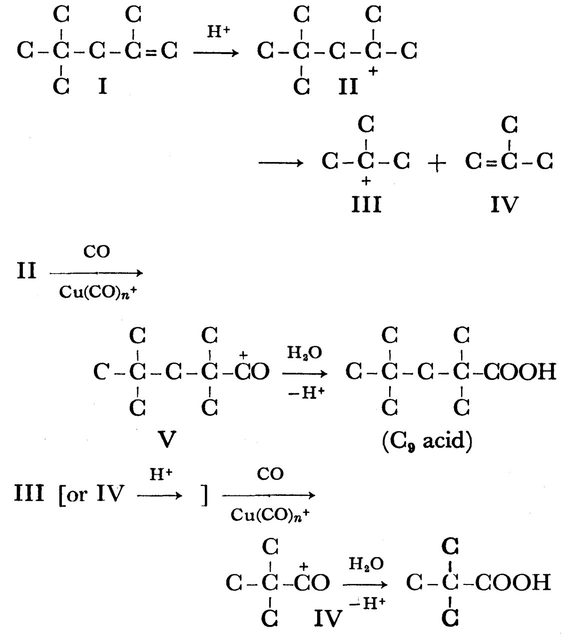
The value of CO(absorbed)/Ag(I) becomes 2 in the H_2SO_4–$1/4SO_3$ at −10 °C under a carbon monoxide pressure of 20 kg/cm^2 for silver carbonyl, which is also expected to have the same catalytic activity for the carboxylation of olefins.[6)] However, such dicarbonyl silver(I) cation was readily prepared in BF_3–H_2O (0.9: 1 molar ratio) under atmospheric pressure (Fig. 1).

The Cu(I) carbonyl cation with high carbon monoxide coordination can be expected to show a much higher catalytic activity in the carboxylation reaction of olefins. Matsushima *et al.* first reported[7)] the formation of tetracarbonylcopper(I) cation, $Cu(CO)_4^+$, in BF_3–H_2O (1: 1.06 molar ratio) solution. However, no investigation seems to have been carried out on the carboxylation of olefins using such acid media involved Ib group metal carbonyl cation before we presented our data.[3)]

Reaction of 2,4,4-Trimethyl-1-pentene (Diisobutylene) with Carbon Monoxide in Various Acids–H_2O Containing Copper or Silver Carbonyl Cations. Carboxylation of 2,4,4-trimethyl-1-pentene (TMP) with carbon monoxide was carried out in the presence of BF_3–H_2O, BF_3–H_3PO_4–H_2O, BF_3–H_2SO_4–H_2O, BF_3–HF–H_2O and HF–H_2O having copper carbonyl cation with cyclohexane or chlorobenzene as a co-solvent at 18—30 °C. The results are summarized in Table 1.

The reaction took place in two liquid phase system (upper solvent layer and lower catalyst layer). The carboxylic acids produced were usually present in both layers. The total yield of carboxylic acids, *i.e.*, the sum of yields in both layers, was found to be considerably higher than that obtained in 96% H_2SO_4.

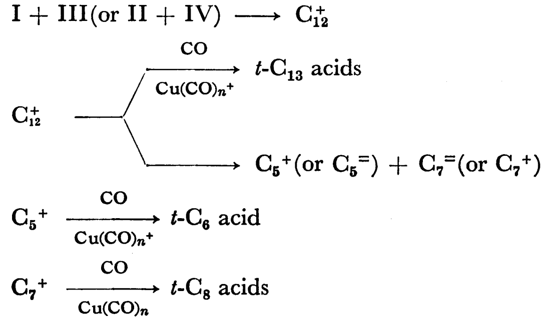
The carboxylic acids thus obtained consist of 2,2-dimethylpropanoic acid and C_9 acids together with small amounts of C_6—C_8 and other acids. Thus, the reaction of TMP with carbon monoxide in the presence of acid–H_2O–group Ib metal carbonyl, is considered to proceed as shown in the following scheme.



$$\text{C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-C-}\overset{\text{C}}{\text{C}}\text{=C}\ \text{I} \xrightarrow{H^+} \text{C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-C-}\overset{\text{C}}{\underset{+}{\text{C}}}\text{-C}\ \text{II} \longrightarrow \text{C-}\overset{\text{C}}{\underset{+}{\text{C}}}\text{-C}\ (\text{III}) + \text{C=}\overset{\text{C}}{\text{C}}\text{-C}\ (\text{IV})$$

$$\text{II} \xrightarrow[Cu(CO)_n^+]{CO} \text{C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-}\overset{+}{\text{CO}}\ (\text{V}) \xrightarrow[-H^+]{H_2O} \text{C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-COOH}\ (C_9\ \text{acid})$$

$$\text{III [or IV} \xrightarrow{H^+} \text{]} \xrightarrow[Cu(CO)_n^+]{CO} \text{C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-}\overset{+}{\text{CO}}\ \text{IV} \xrightarrow[-H^+]{H_2O} \text{C-}\overset{\text{C}}{\underset{\text{C}}{\text{C}}}\text{-COOH}$$



The tertiary C_9 acids of various skeletal structures were found in the products, since skeletal isomerization of C_8 carbenium ion (II) takes place easily under such reaction conditions.

The carboxylic acids existing in the solvent layer seem to be produced by the reaction of alkanoyl cations such as V and VI with water in the catalyst, *i.e.*, acid–H_2O–$Cu(CO)_n^+$. Such carboxylic acids were obtained in a high yield in the presence of BF_3–H_2O–$Cu(CO)_n^+$ catalyst. Despite the fact that an almost quantitative total yield of carboxylic acid was obtained in the presence of HF–H_2O–$Cu(CO)_n^+$ or HF–H_2O–BF_3–$Cu(CO)_n^+$, an insufficient amount of carboxylic acids separated into the organic layer under the conditions employed.

Carboxylation of Trimethylpentene Using BF_3–H_2O–$Cu(CO)_n^+$ Catalyst. Carboxylation of TMP with carbon monoxide was studied in the presence of BF_3–H_2O–$Cu(CO)_n^+$ with various BF_3/H_2O molar ratios. The results are given in Table 2.

TABLE 2. EFFECT OF BF_3/H_2O MOLAR RATIO OF BF_3–H_2O ON THE REACTION

BF_3–H_2O	Total yield of acid, % (acid value)	Product distribution (%)	
BF_3/H_2O Molar ratio		Yield of acid found separately from cat. layer (acid value)	Yield of acid found in cat. layer (acid value)
0.6	12.7(366)	97.0(366)	3.0(—)
0.7	47.8(362)	93.8(356)	6.2(461)
0.8	79.0(371)	86.5(356)	13.5(467)
0.9	76.9(395)	62.7(347)	37.3(478)
1.0	80.4(375)	59.9(344)	40.1(440)

Reaction conditions: BF_3, 0.50 mol; Cu_2O, 14 mmol: reaicton temperature, 30 °C, trimethylpentene, 0.10 mol.

The total yield of carboxylic acids increased with increase in the BF_3/H_2O molar ratio of the catalyst. An important feature is that the reaction takes place with the release of a large portion of the carboxylic acids as products from the catalyst layer without addition of water at the end of the reaction. The portion of carboxylic acids thus obtained was found to be over 90% of all the products in the presence of the catalyst having a BF_3/H_2O molar ratio less than 0.7. However, this portion tends to decrease with increase in the BF_3/H_2O molar ratio of the catalyst.

The BF_3–H_2O complex with BF_3/H_2O molar ratio of 1 is known as a stronger acid than concentrated sulfuric acid (96%) and can be described as $H^+BF_3OH^-$. The Ho value of this acid was reported to be −11.4 (Ho of 100% H_2SO_4 is −11.2).[8] The complexes with BF_3/H_2O molar ratio in the range 0.5—1.0 are mainly mixture of $H^+BF_3OH^-$ and $H_3^+OBF_3OH^-$.[9] The latter species (boron trifluoride dihydrate) should be a weaker acid than the former.

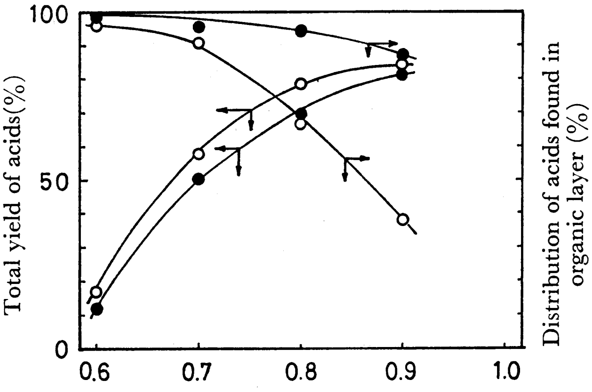
$$BF_3 + H_2O \rightleftharpoons H^+BF_3OH^-$$

$$H^+BF_3OH^- + H_2O \rightleftharpoons H_3^+OBF_3OH^-$$

The content of $H^+BF_3OH^-$ increases with increase in BF_3/H_2O.[10] $H^+BF_3OH^-$ appears to have a stronger affinity for carboxylic acids than $H_3^+OBF_3OH^-$. Hence, in the case of a catalyst rich in $H^+BF_3OH^-$, most of the carboxylic acids produced would be readily protonated to form $RCOOH_2^+BF_3OH^-$ and remain in the catalyst layer. However, when we use catalysts rich in $H_3^+OBF_3OH^-$, most of the carboxylic acids are present in the form of free acid and can be found separately from the catalyst layer.

Higher carboxylic acids such as C_9 and C_{13} acids might have smaller affinity for the catalyst as compared with lower ones such as 2,2-dimethylpropanoic acid, since the mean acid value of the products found in the catalyst layer is always higher than that of those obtained separately from the catalyst layer (Table 2).

The reaction may be expected to occur effectively by separating the products and catalyst from each other with heterogeneous use of co-existing organic solvents.



BF_3/H_2O molar ratio

Fig. 2. The effect of BF_3/H_2O molar ratio of BF_3–H_2O on the total yield of acids and distribution of acids found in organic layer.
Reaction conditions: BF_3, 0.50 mol; Cu_2O, 14 mmol; reaction temperature, 30 °C; trimethylpentene, 0.10 mol; organic solvent, 50 ml.
-●-: Chlorobenzene, -○-: cyclohexane.

A solution of TMP in cyclohexane or chlorobenzene was added dropwise to the BF_3–H_2O–$Cu(CO)_n^+$ catalyst with a 0.6—0.9 BF_3/H_2O molar ratio, carbon monoxide being introduced at 30 °C. The results are shown in Fig. 2. All the reactions took place in the heterogeneous liquid phase to give products present in the organic and catalyst layers. The total yield of acids was found to be almost the same as in the case where no organic solvent was used. However, the amount of acids found in the organic layer was greatly affected by the BF_3/H_2O molar ratio in the catalyst, particularly in the case of cyclohexane.

TABLE 3. EFFECT OF ORGANIC SOLVENTS ON THE CARBOXYLATION OF TRIMETHYLPENTENE

Organic solvent	Total yield of acids %	Acids found in organic layer %	Composition of acid products											
			Acids in total				Acids in org. layer				Acids in cat. layer			
			C_5	C_{6-8}	C_9	C_{others}[a)]	C_5	C_{6-8}	C_9	C_{others}[a)]	C_5	C_{6-8}	C_9	C_{others}[a)]
Non	76.9	62.7	31.7	13.3	36.1	18.9	16.6	11.6	42.0	29.8	57.0	16.2	26.1	0.7
Cyclohexane	82.1	36.5	41.0	13.9	35.5	9.6	8.9	8.6	59.0	24.0	62.5	17.6	20.2	—
Mesitylene	84.6	69.0	26.1	10.9	50.4	12.6	12.8	10.1	60.4	16.7	56.3	12.7	27.7	3.3
Chloro-Cyclohexane	49.8	82.3	13.5	11.1	35.5	39.9	8.6	11.0	37.1	43.3	35.6	11.8	28.1	24.5
Fluorobenzene	80.4	79.9	40.7	9.9	40.6	8.8	30.8	10.4	48.4	10.4	80.2	7.8	9.3	2.7
Chlorobenzene	80.1	84.5	44.2	10.7	36.1	9.0	37.1	11.4	41.0	10.5	83.1	7.0	9.3	0.6
Bromobenzene	71.2	82.5	34.9	12.0	44.0	9.1	26.6	12.4	50.2	10.8	73.3	9.7	15.6	1.4
CCl_4	72.9	—	44.4	11.4	34.7	9.5	—	—	—	—	—	—	—	—
$CHCl_3$	66.7	94.4	40.3	7.7	40.4	11.6	38.0	7.7	42.2	12.1	78.5	7.5	10.4	3.6
CH_2Cl_2	46.4	96.5	30.6	19.5	36.3	13.6	29.2	19.7	13.1	14.0	69.7	13.6	13.7	3.0
CH_2ClCH_2Cl	54.1	93.5	35.8	15.1	42.2	6.9	33.0	15.4	44.7	6.9	76.5	11.6	4.4	7.5

a) Polymeric acids. b) Reaction conditions: BF_3–H_2O, 40 g; BF_3/H_2O molar ratio, 0.9; Cu_2O, 14 mmol; reaction temperature, 30 °C; olefin, 0.10 mol; organic solvent, 50 ml.

Other organic solvents were also examined by using the BF_3–H_2O complex with a 0.9 BF_3/H_2O molar ratio (Table 3). The products were again found in both layers except for the case using tetrachloromethane which resulted in an emulsion. The product distribution between both layers was greatly affected by the kind of solvent.

A significant quantity of the product was found to be distributed in organic solvents such as polyhalogenated alkyl compounds. However, the total yield of carboxylic acid produced was rather low as compared with the case in which no solvent reaction took place. In the course of the reaction using these solvents, the formation of copper carbonyl chloride Cu(CO)Cl, which has no catalytic activity, was observed. This is shown in the following scheme for the case of chloroform.

$$CHCl_3 \rightleftarrows \overset{+}{C}HCl_2 + Cl^-$$

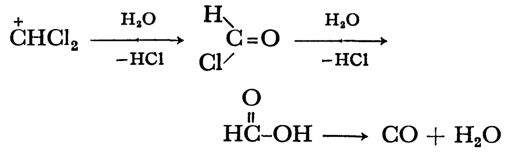
$$Cu(CO)_n^+ + Cl^- \longrightarrow Cu(CO)Cl + (n-1)CO$$

Although chloroform is known to easily undergo hydrolysis in basic solution, hardly any report is available on its behavior in acidic media.[11,12)] However, the reaction of chloroform with aromatic compounds forming triarylmethane is known to be induced by a Lewis acid such as aluminum chloride, iron(III) chloride and so on. Thus the free form of BF_3 liberated in the BF_3–H_2O solution can also be considered to be a catalyst which induces the formation of active species as shown in the following.

$$CHCl_3 + BF_3 \longrightarrow \overset{+}{C}HCl_2BF_3Cl^-$$

This species might be considered to be the source of chloride anion and $\overset{+}{C}HCl_2$ cation.

We examined the behavior of chloroform in BF_3–H_2O solution by adding silver nitrate. In a solution allowed to stand at room temperature with stirring, the formation of silver chloride was observed with the evolution of carbon monoxide.[12)] From the results, it seems that chloroform in the BF_3–H_2O liberates chloride anion and $\overset{+}{C}H_2Cl$ cation which undergo hydrolysis to give formic acid and then decompose into water and carbon monoxide.



$$\overset{+}{C}HCl_2 \xrightarrow[-HCl]{H_2O} \begin{matrix}H\diagdown\\ C=O\\ Cl\diagup\end{matrix} \xrightarrow[-HCl]{H_2O} H\overset{O}{\overset{\|}{C}}\text{-}OH \longrightarrow CO + H_2O$$

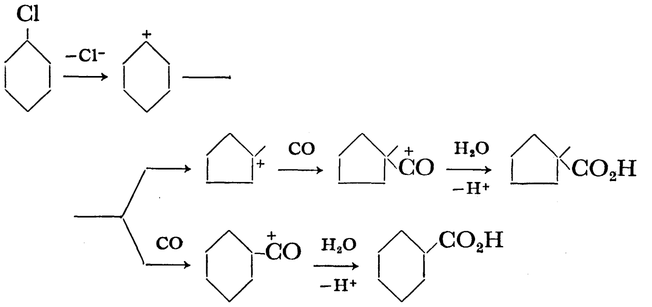
In the presence of cyclohexane, mesitylene or halobenzenes, the reactions give satisfactory high yields of carboxylic acids (Table 3).

The amount of products in the cyclohexane layer is extremely low as compared with the cases using other organic solvents. This is puzzling. The amount of acid products in the organic layer would be affected by the product composition obtained by the reaction. Namely, the reactions producing rather long chain carboxylic acids with less affinity for the catalyst should give large amounts of products in the organic solvent layer. Although C_5 acids and C_9 acids are the main products in each case, C_6, C_8 and longer chain acids than C_{13} were produced. These carboxylic acids are formed as follows. TMP is depolymerized by acid to give 2-methylpropene and *t*-butyl cation which in turn reacted with another molecule of TMP to form C_{12}^+ or higher cations. On the other hand, C_5^+ and C_7^+ ions are produced by the depolymerization of C_{12}^+ (Scheme 1). In the case of the reaction using a higher acidic catalyst such as one with a 0.9 BF_3/H_2O molar ratio, it is particularly easy to form C_{12}^+ and longer chain carbocations which would be sources of long chain carboxylic acids.

Thus, dilution of the alkene by an organic solvent would more or less prevent the formation of longer acids. This is the case where the reaction in the presence of cyclohexane gave rise to the formation of C_{13} and higher acids in rather low yields in the composition, most of the 2,2-dimethylpropanoic acid in high yields remaining in the catalyst layer.

Such a tendency was clearly seen in the reactions using BF_3–H_2O acid systems with large BF_3/H_2O molar ratios. The reaction in the presence of lower acidic catalyst of BF_3–H_2O with BF_3/H_2O molar ratio of 0.7 or less gave C_9 acids as the main products which were in the organic solvent layer as shown in Fig. 2.

However, as seen in Table 3, although almost the same composition of products was obtained when cyclohexane and halobenzenes were used as the solvent, the amount of products found in the halobenzene layer was always higher. The solubility of carboxylic acids in such organic solvents may be different. In fact, we found that cyclohexane shows a lower solubility for 2,2-dimethylpropanoic acid at 10 °C (1.07 g/ml) than other solvents (chlorobenzene, 1.34 g/ml; chloroform, 1.44 g/ml). Thus, chlorocyclohexane which has a high solubility for 2,2-dimethylpropanoic acid (1.8 g/ml) should dissolve acid products. However, a remarkable formation of other acids was observed. This might be due to the occurrence of a side-reaction, as shown in the following equation. Cl^- liberated in the course of the reaction should deteriorate the catalyst.



The effect of reaction temperature on the yield of carboxylic acids was also examined. The results are shown in Figs. 3 and 4.

The reaction using 96% H_2SO_4 gave a 56% maximum total yield of products at 40 °C, the catalytic activity decreasing thereafter rapidly because of the decomposition of Cu(I) carbonyl cation. On the other hand, the reaction using BF_3–H_2O complex gave the products in *ca.* 20% yield even at 70 °C. This seems also to indicate

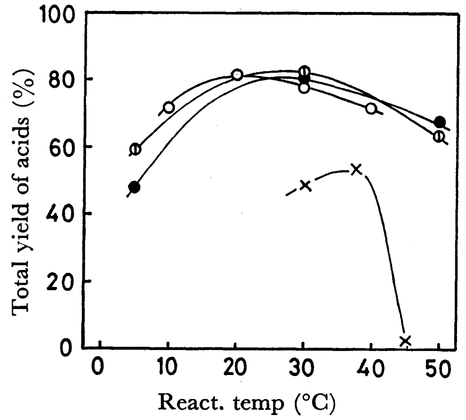


Fig. 3. The effect of reaction temperature on the total yield of acids.
Reaction conditions: BF_3–H_2O, 24 g; BF_3/H_2O molar ratio, 0.90; 96% H_2SO_4, 40 g; Cu_2O, 14 mmol; reaction time, 30 min; amount of solvent, 50 ml; trimethylpentene, 0.10 mol.
-×-: 96% H_2SO_4, -○-: without solvent, -●-: chlorobenzene, -⦶-: cyclohexane.

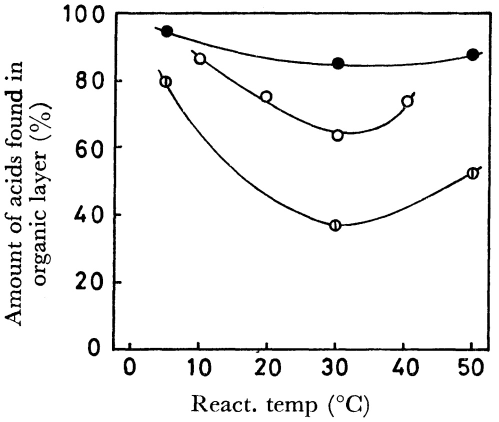


Fig. 4. The effect of reaction temperature on the amount of acids found in organic layer.
Reaction conditions: BF_3–H_2O, 24 g; BF_3/H_2O molar ratio, 0.9; Cu_2O, 14 mmol; reaction time, 30 min; amount of solvent, 50 ml; trimethylpentene, 0.10 mol.
-○-: Without solvent, -●-: chlorobenzene, -⦶-: cyclohexane.

the high stability of active species as catalyst, *i.e.*, $Cu(CO)_3^+$ in the BF_3–H_2O complex in a wide range of temperature.

The reaction using BF_3–H_2O complex in the presence of chlorobenzene showed no large difference in yield of acid products found in the organic layer over the entire range of reaction temperature (Fig. 4). However, in the presence of cyclohexane, or in the absence of organic solvent, the amount of such products found to be remarkably decreased at 30 °C. The reactions under these conditions have a tendency to form products rich in 2,2-dimethylpropanoic acid with a high affinity to the catalyst layer. In the reactions carried out at low reaction temperatures, polymerization and depolymerization of TMP resulting in the formation of C_{13} or higher carboxylic acids would be predominant. These long chain carboxylic acids clearly have less affinity to the catalyst and should exist apart from the catalyst layer. In reactions at a temperature higher than 40 °C, the rate of reaction of carbon monoxide with 1,1,3,3-tetramethylbutyl cation derived from initial protonation of TMP would cause a β-cleavage of the cation to give *t*-butyl cation and 2-methylpropene. Hence, the reaction gave products rich in C_9 acids, most of them being observed in the organic layer because of the low affinity of C_9 acids to the catalyst layer.

Repeated Use of the Catalyst. In order to show the advantage of a Cu(I)–carbonyl catalyst in the BF_3–H_2O solution, we have extended our investigation to recycling of the used catalyst. The carboxylation of olefins in various organic solvents was conducted in the same way as described in the previous section. After completion of the reaction, the recovered catalyst layer which had been added to the corresponding amount of water consumed in the first run was used for the second run under the same conditions. The upper organic solvent layer separated out from the reaction mixture was subjected to work-up for the product and analysis for the amount of copper ion as Cu^{2+} after oxidation with

TABLE 4. REPEATED USE OF THE CATALYST (BF_3/H_2O= 0.9) IN THE CARBOXYLATION OF TRIMETHYLPENTENE (solvent; cyclohexane)

No. of repeated expt.	Yield of acid$^{a),d)}$ %	Product distribution$^{a)}$ %				Cu^{2+} mg
		C_5	C_{6-8}	C_9	C_{others}	
1	24	17	8	56	19	trace
2	30	—	—	—	—	trace
3	41	11	9	45	35	trace
4	32	—	—	—	—	trace
5	49	14	11	43	32	trace
	(—$^{c)}$	44	16	28	12)$^{b)}$	

a) Found in organic layer in each expt. b) Product distribution found in catalyst layer in the 5th expt. c) The acids found in the catalyst layer was 55% of total yields of acids. d) Total yield of acids 77%. Reaction conditions: initial amount of BF_3–H_2O, 62 g; Cu_2O, 14 mmol; react. temp 30 °C; olefin 0.1 mol; solvent, 50 ml, in each run.

TABLE 5. REPEATED USE OF THE CATALYST (BF_3/H_2O= 0.7) IN THE CARBOXYLATION OF TRIMETHYLPENTENE (solvent; cyclohexane)

No. of repeated expt.	Yield of acid$^{a),d)}$ %	Product distribution$^{a)}$ %				Cu^{2+} mg
		C_5	C_{6-8}	C_9	C_{others}	
1	54	22	16	56	6	trace
2	56	26	15	52	7	trace
3	45	25	13	56	6	trace
4	57	21	14	56	9	trace
5	56	25	15	50	10	trace
	(—$^{c)}$	66	17	16	1)$^{b)}$	

a) Found in organic layer in each expt. b) Product distribution found in catalyst layer in the 5th expt. c) The acids found in the catalyst layer was 6% of total yield of acids. d) Total yield of acids, 57%. Reaction conditions: initial amount of BF_3–H_2O, 68 g; Cu_2O, 14 mmol; react. temp, 30 °C; olefin, 0.1 mol; solvent 50 ml in each run.

TABLE 6. REPEATED USE OF THE CATALYST (BF_3/H_2O= 0.9) IN THE CARBOXYLATION OF 1-OCTENE (solvent; cyclohexane)

No. of repeated expt.	Yield of acid$^{a),d)}$ %	Product distribution$^{a)}$ %				Cu^{2+} mg
		C_5	C_{6-8}	C_9	C_{others}	
1	73	3	0.2	97	—	trace
2	69	1	—	99	—	trace
3	72	1	—	99	—	trace
4	67	—	—	100	—	trace
5	65	—	—	100	—	trace
	(—$^{c)}$	11	1	88	—)$^{b)}$	

a) Found in organic layer in each expt. b) Product distribution found in catalyst layer in the 5th expt. c) The acids found in the catalyst layer was 1.5% of total yield of acids. d) Total yield of acids, 70%. Reaction conditions: initial amount of BF_3–H_2O, 62 g; Cu_2O, 14 mmol; react. temp, 30 °C; olefin, 0.1 mol; solvent, 50 ml in each run.

TABLE 7. REPEATED USE OF THE CATALYST (BF_3/H_2O= 0.9) IN THE CARBOXYLATION OF TRIMETHYLPENTENE (solvent, chlorobenzene)

No. of repeated expt.	Yield of acid$^{a),d)}$ %	Product distribution$^{a)}$ %				Cu^{2+} mg
		C_5	C_{6-8}	C_9	C_{others}	
1	64	38	21	41	1	69
2	69	—	—	—	—	105
3	73	—	—	—	—	330
4	83	32	13	40	15	340
5	98	—	—	—	—	475
6	68	25	14	39	22	375
	(—$^{c)}$	43	19	33	5)$^{b)}$	

a) Found in organic layer in each expt. b) Product distribution found in catalyst layer in the 6th expt. c) The acids found in the catalyst layer was 1.5% of total yield of acids. d) Total yield of acids, 77%. Reaction conditions: initial amount of BF_3–H_2O, 62 g; Cu_2O, 14 mmol; react. temp, 30 °C; olefins, 0.1 mol; solvent, 50 ml in each run.

air by the usual atomic absorption spectroscopic method.[13] Some typical results are given in Tables 4—7.

In the reaction of TMP using cyclohexane as a solvent, the activity of catalyst remained unchanged. Only a negligible amount of copper ion was present in the organic solvent layer (Tables 4 and 5).

A gradual accumulation of carboxylic acid was observed in the catalyst layer with successive use of the catalyst. In the case of BF_3–H_2O with a 0.9 molar ratio (Table 4), *ca.* 55% of the total yield of carboxylic acids was found in the catalyst layer after five repeated runs. However, this accumulation of products in the catalyst layer was remarkably decreased when a catalyst with 0.7 BF_3/H_2O molar ratio was used. Only 6% of carboxylic acids was present (Table 5).

In the reaction of 1-octene, there was no accumulation of products in the catalyst layer even in the case of BF_3–H_2O with 0.9 molar ratio (Table 6). Since no cleavage of carbon-carbon bonds in the olefin takes place, almost all the carboxylic acids produced were C_9-acids which have less affinity to the catalyst layer.

On the other hand, in the reaction of TMP using chlorobenzene as a solvent, almost complete recovery of products into the solvent layer was observed even in the presence of the catalyst with 0.9 BF_3/H_2O molar ratio (Table 7). In contrast, the amount of copper ion found in the organic layer was considerably high. This might decrease the concentration of the active species by successive use of the catalyst layer.[14]

The present procedure seems to have a great advantage in the practical preparation of carboxylic acids by carboxylation of olefins with carbon monoxide.

References

1) Y. Souma, H. Sano, and J. Iyoda, *J. Org. Chem.*, **38**, 2016 (1973); Y. Souma and H. Sano, *Bull. Chem. Soc. Jpn.*, **46**, 3237 (1973).

2) H. Koch, *Brennstoff-Chemie*, **36**, 321 (1955); H. Koch and W. Haaf, *Justus Liebigs Ann. Chem.*, **618**, 251 (1958); K. E. Möller, *Brennstoff-Chemie*, **47**, 10 (1966).

3) N. Yoneda, T. Fukuhara, Y. Takahashi, and A. Suzuki, *Chem. Lett.*, **1974**, 607.

4) M. Matsubara, Y. Matsushima, N. Yoneda, and H. Ohtsuka, *Kogyo Kagaku Zasshi*, **73**, 2147 (1970); N. Yoneda, Y. Matsushima, M. Matsubara, and H. Ohtsuka, *Bull. Jpn. Petrl. Inst.*, **14**, 178 (1972).

5) H. Sano, *Nippon Kagaku Kaishi*, **1970**, 630.

6) Y. Souma and H. Sano, *Chem. Lett.*, **1973**, 1059.

7) Y. Matsushima, T. Koyano, T. Kitamura, and S. Wada, *Chem. Lett.*, **1973**, 433.

8) N. Yoneda and Y. Takahashi, *J. Jpn. Petrl. Inst.*, **20**, 468 (1977).

9) N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, **1951**, 1915.

10) N. Yoneda and H. Ohtsuka, *Kogyo Kagaku Zasshi*, **72**, 1743 (1969).

11) J. March, "Advanced Organic Chemistry," McGraw-Hill Book Co. (1968), p. 304.

12) $CHCl_3$ in concentric sulfuric acid with silver nitrate did not react under such conditions.

13) T. Takeuchi and M. Suzuki, "Genshikyuko Bunko Bunseki," Nankodo (1972).

14) When the organic layer thus obtained was treated with aqueous alkaline solution, yellow precipitate of copper hydroxide was formed, the amount of which corresponds to that of Cu^{2+} determined by atomic absorption spectroscopy. Cu(I) carbonyl solubilized into organic layer could be recovered as cuprous oxide after calcination of copper hydroxide in the absence of oxygen.